

Graft and Block Copolymers of Some Vinyl Aromatic Hydrocarbons*

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I. INTRODUCTION

The aromatic moieties of vinyl polymers such as polyvinylbiphenyl and polyvinyl-naphthalene react in solution with alkali metals to form colored charge transfer complexes referred to as polyradicalanions.¹ These initiate the polymerization of ethylene oxide by bond formation thus leading to graft polymers. Experimental evidence for bond formation was obtained with the biphenyl and naphthalene molecules. The position of attack of substituted aromatic rings by ethylene oxide could be correlated with calculated π -electron densities. The calculations were carried out using the HMO approximation and allowing for the induction effect of substituents. In order to establish optimum conditions for graft formation a study was made of the stability of several polyradicalanion species. The polyradicalanions undergo chain scission at ambient temperature by a mechanism which involves electron localization on the aliphatic α -carbon atom and, ultimately, formation of carbanionic chain ends. The relative stabilities of the aromatic systems considered are related to the π -energy changes involved in the bond scission reaction.

Graft and block copolymers having a backbone of poly-4-vinylbiphenyl (PVB) or poly-2-vinylnaphthalene (PVN) and branches of polyethylene oxide (PEO), were prepared. These polymers were characterized by their solubility behavior as well as by chemical and spectral analyses. Torsional modulus versus temperature determinations provided information about the mechanical properties and glass transition temperatures of these materials. Comparisons were made with the behavior of the homopolymers and their blends.

II. EXPERIMENTAL

1. Purification of Materials

4-Vinylbiphenyl and 2-vinylnaphthalene were purified by passing each monomer in benzene and *n*-hexane solution (50 wt.-%) through a column

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of activated alumina. After rejecting the first fraction (10% of the monomer by weight), eluting with pure benzene, and evaporating the solvent, the monomers were crystallized from methanol and dried. 4-Vinylbiphenyl melted at 117°C. and 2-vinylnaphthalene at 65°C.

Ethylene oxide was distilled from solid caustic potash into glass ampules through a column filled with glass beads covered with a thin film of sodium.

Tetrahydrofuran (THF) was purified by reacting it with a sodium potassium alloy and then distilling from a sodium mirror.

2. Anionic Polymerization of 4-Vinylbiphenyl

4-Vinylbiphenyl reacted with sodium in THF was used as initiator. The polymerization technique in high vacuum was previously described.² Using decreasing amounts of initiator, molecular weights of 70,000 to 500,000 were obtained. The weight-average molecular weights (\bar{M}_w) were estimated from a previously determined relationship.³

3. Emulsion Polymerization

Larger quantities of both PVB and PVN were prepared by emulsion polymerization in the following way. 2-Vinylnaphthalene (20 g.), distilled water (500 ml.), potassium persulfate (0.01 g.), and Triton X-100 (0.5 g.) were stirred in a nitrogen atmosphere at 95°C. for 7 hr. The formed polymer was filtered, dried, redissolved in benzene, precipitated with methanol, filtered, and dried at 60°C. in a vacuum oven for 14 hr.; yield 12.7 g.

The intrinsic viscosity in benzene was 1.17; the estimated⁴ molecular weight was 950,000. 4-Vinylbiphenyl polymerized in an identical way yielded a polymer with $[\eta] = 0.73$ ($\bar{M}_w = 460,000$).

4. Graft Formation

All operations were carried out in dry glass apparatus and all reagents thoroughly degassed under a pressure of 10^{-5} mm. Hg. The technique for transfer of reagents and preparation of metallic cesium was already described.² PVB or PVN dissolved in THF reacted with a cesium mirror at -80°C. to give blue and green solutions, respectively. After addition of ethylene oxide the temperature was raised to 0°C. The mixture became viscous within 30 min. to 4 hr. and was kept for 24 hr. at room temperature to assure complete reaction. The anionic chain ends were deactivated by 0.5 ml. of methanol or methyl iodide; *n*-hexane was then added, and the polymer filtered and dried in vacuum. 100% yields were obtained in all experiments.

5. Block Formation

A PVB-EO block polymer was prepared by a method similar to the one used for the preparation of polystyrene-ethylene oxide blocks.⁵ 4-Vinylbiphenyl was polymerized using cesium initiation as described previously,²

and ethylene oxide was added at 0°C. The subsequent steps were identical to the procedure described above for graft formation.

6. Characterization of Products

a. Analyses. The weight per cent PVB in a water-extracted graft polymer was determined by using the extinction coefficient of PVB at 254 $m\mu$ found to be equal to 110 l./g.-cm. in dimethoxyethane. The PEO content was determined from the extinction coefficient of pure PEO at 9 μ in chloroform. A calibration curve (Fig. 1) was established by means of PEO-PVB blends of known concentration. Similarly the analysis of PVN was based on the extinction coefficient of pure PVN at 278 $m\mu$ found to be equal to 29.3. Visible spectra were recorded on a Beckman DK2, and the ultraviolet and infrared analyses were carried out by means of a Beckman D.U. and Perkin-Elmer Model 21 spectrophotometer, respectively. Both analytical methods are accurate to $\pm 5\%$. The cesium con-

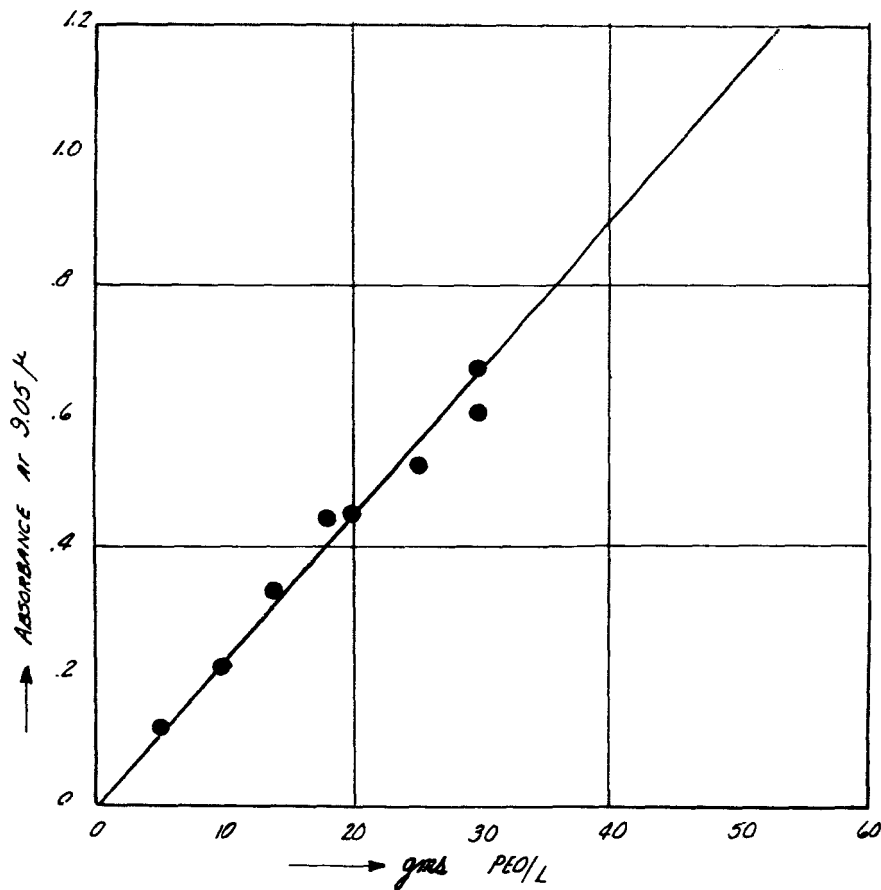


Fig. 1. Absorbance of PVB-PEO synthetic mixtures in chloroform.

centration was determined either by direct titration with 0.1N HCl with phenolphthalein as indicator or by titration of NaI, after termination of the active chain ends with methyl iodide. The latter method yielded alkali concentrations 10 to 20% lower than the direct titration procedure.

b. Viscosity. Viscosities of isolated polymer were determined in an Ubbelohde viscometer in benzene at $25 \pm 0.5^\circ\text{C}$. Flow times of polyradicalanions in THF and of solvent were determined in a Cannon Zhukov viscometer, which was modified to enable the determination of viscosities in the absence of air.

c. Young's Modulus. Estimations of Young's modulus were made on a torsional apparatus constructed according to A.S.T.M. standards.⁶

d. ESR Spectra. Electron spin resonance spectra were obtained by means of the 4500 Varian Associates spectrometer on samples dissolved in THF and placed in evacuated quartz or Pyrex glass tubes (4 m. O.D.).

e. Film Molding. The polymer films were prepared by compression of powdered samples between 2,000 and 10,000 psi at temperatures characteristic of the polymer. For PEO and unextracted graft polymer the temperature was 62°C ., for pure PVB and PVN 150°C ., and for the extracted grafts 105°C .

III. RESULTS

1. Stability of Polyradicalanions and Polymeric Anions

a. Decrease of Viscosity and Molecular Weight. The reduced specific viscosities of PVB and PVN as a function of temperature and time are shown in Figures 2 and 3, respectively.

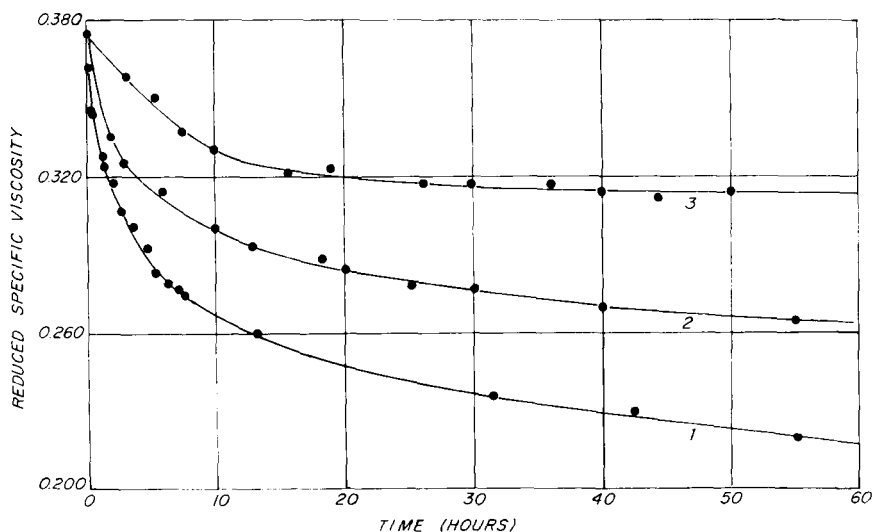


Fig. 2. Reduced specific viscosity of PVB ($\bar{M}_w = 184,000$) vs. time: (1) sodium concentration $3 \times 10^{-2}M$, temperature 50°C .; (2) sodium concentration $7 \times 10^{-3}M$, temperature 50°C .; (3) sodium concentration $2.5 \times 10^{-3}M$, temperature 25°C .

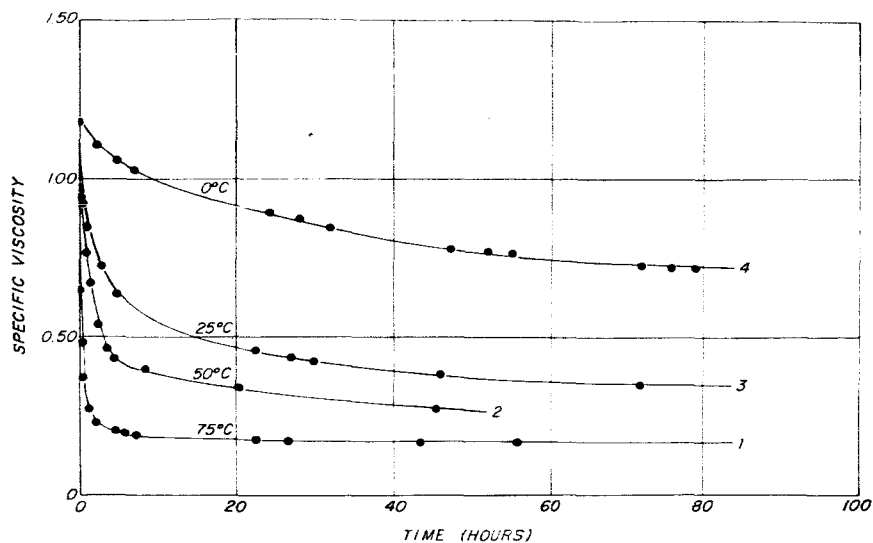


Fig. 3. Specific viscosity of PVN ($\bar{M}_w \approx 950,000$) vs. time at several temperatures at sodium concentration $8 \times 10^{-3}M$: (1) $75^\circ C$.; (2) $50^\circ C$.; (3) $25^\circ C$.; (4) $0^\circ C$.

Table I shows the actual molecular weight of polymers isolated at various times. Neither PVB nor the PVN complex was degraded when kept at $-20^\circ C$. for 4 hr. In contrast to polyradicalanions, the long-chain anions

TABLE I
Molecular Weights of PVB Polyradicalanion as a Function of Time

Polymer concentration, g./l.	Sodium concentration, mmoles/l.	Temperature, $^\circ C$.	Time, hr	Intrinsic viscosity (in benzene)	\bar{M}_w
40	4	25	0	0.731	440,000
40	4	25	4	0.568	320,000
40	4	25	232	0.465	250,000

TABLE II
Degradation of PVB Anions with Time

Sample	Sodium concentration, mmoles/l.	Polymer concentration, g./l.	Temperature, $^\circ C$.	Time, hr.	Intrinsic viscosity (in benzene)	Weight-average molecular weight \bar{M}_w
1	7	80	50	0	0.257	100,000
1	7	80	50	24	0.256	100,000
1	7	80	50	200	0.257	100,000
2	3	80	100	0	0.716	455,000
2	3	80	100	24	0.654	390,000
2	3	80	100	264	0.564	330,000

formed by reaction of sodium naphthalene or sodium with 4-vinylbiphenyl were found to be relatively stable. No change in the intrinsic viscosities took place at 50°C. after 200 hr. of heating. Significant degradation, however, occurred at 100°C. (Table II).

b. Color and Visible Spectra. The blue color of PVB polyradicalanions persisted at -80°C. for several days. Above 50°C., however, it changed to red in a matter of a few hours. This corresponds to an increase of the absorbance in the region characteristic of the dianion, i.e., 425-550 m μ , at the expense of the 400-405 and 605-610 m μ bands characteristic of the radicalanion (Fig. 4), indicating a gradual degradation of the radical anions into polymer anions.

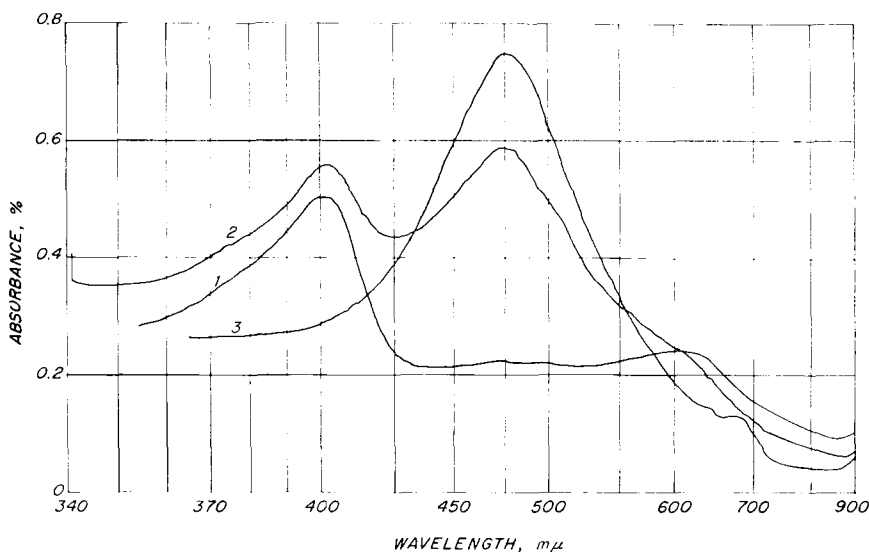


Fig. 4. Spectra of PVB polyradicalanion with time at 50°C.: (1) at zero time; (2) after 2 hr.; (3) after 5 hr.

c. Electron Spin Resonance Spectra. In Figure 5 are shown the spectra of a dilute solution of PVB polyradicalanions when formed and

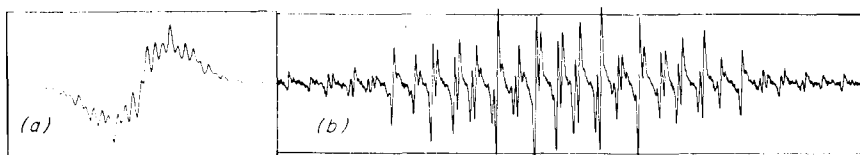


Fig. 5. Electron spin resonance spectrum of PVB on sodium in THF: (a) at zero time; (b) after 14 days at 0°C.

after two weeks at 0°C. In Figure 6 changes in the ESR signals of PVN polyradicalanions kept at 50°C. are recorded with time. It may be seen

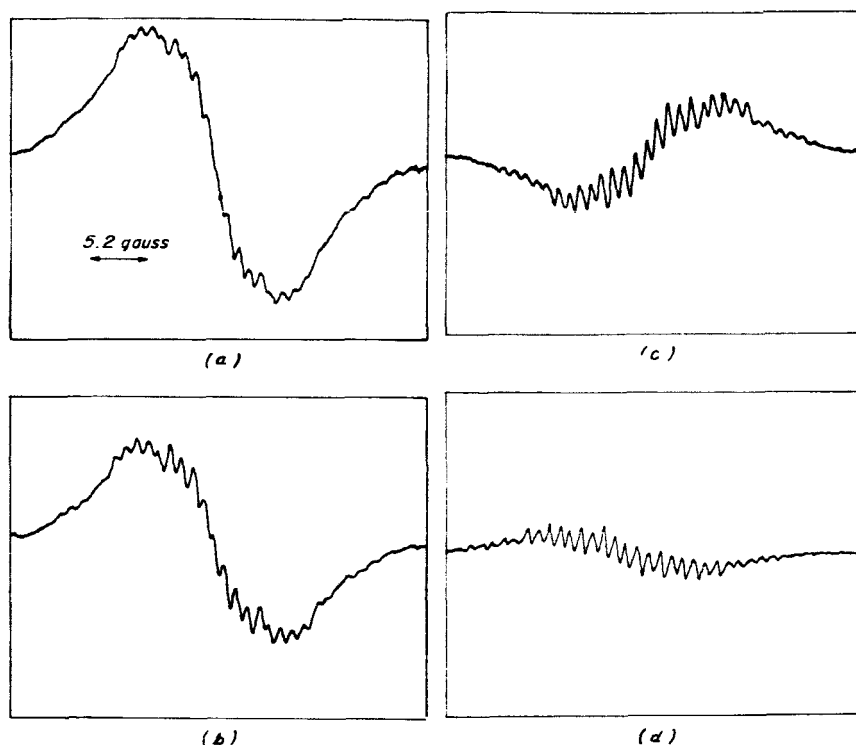


Fig. 6. Electron spin resonance spectrum of PVN on sodium in THF at 50°C.: (a) at zero time; (b) after 40 min.; (c) after 115 min.; (d) after 175 min.

from Figure 6c that a concentrated solution of PVN on sodium gives, after a few hours of heating, a spectrum practically identical to that of the original dilute solution (Fig. 7).

2. Bond Formation

a. Reaction with Carbon Dioxide. THF solutions of complexes of PVB with lithium, sodium, and cesium, respectively, were reacted in the

TABLE III
Analysis of PVB after Reaction with CO₂

Alkaline metal	DP ^a	Analyses ^b			CO ₂ , equiv./chain
		C, %	H, %	O, %	
Na	361	92.98	6.62	0.40	8
Cs	361	93.04	6.77	0.19	4
Na	1000	91.20	6.81	1.99	114
Na	1000	90.74	6.62	2.64	152
Li	361	87.92	6.57	5.51	112

^a Degree of polymerization estimated from intrinsic viscosities $[\eta]$ in benzene.

^b C and H analyses were carried out by Elek Micro-Analytical Laboratories, Los Angeles, California; O was obtained by difference.

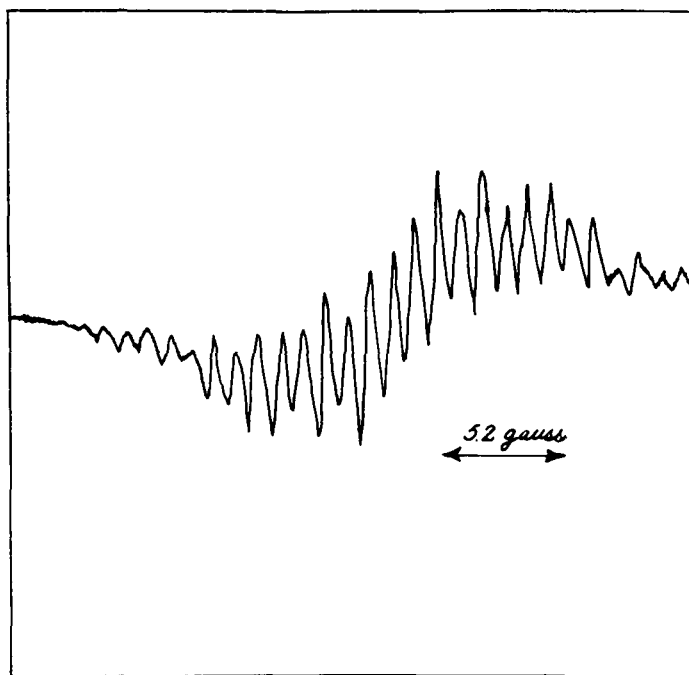


Fig. 7. Electron spin resonance spectrum of a dilute solution of PVN on sodium in THF at zero time before heating.

cold with CO_2 . Incorporation of oxygen into the polymer, as evidenced by elemental analysis (Table III), leaves little doubt that the polyradical-anions reacted with CO_2 to produce carboxylic acids. Assuming that each CO_2 reacted with one biphenyl moiety, then between $1/100$ and $1/3$ of the total biphenyls have been converted to radicalanions. Comparison of infrared absorption spectra (Fig. 8) shows that after the CO_2 reaction two absorption bands appeared at 5.85 and 7.8μ , respectively. The 5.85μ

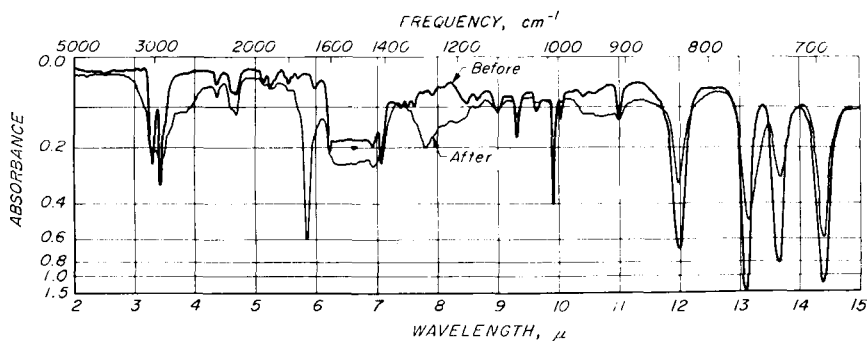


Fig. 8. Absorption spectrum of PVB polyradicalanion before and after reaction with CO_2 in dimethoxyethane (DME).

band is characteristic of CO, and the $7.8\ \mu$ band is attributed to the coupled C—O and OH in-plane deformation modes,⁷ thus giving further evidence for the carboxylation reaction of polyradicalanions.

b. Reaction with Ethylene Oxide. In order to prove bond formation,

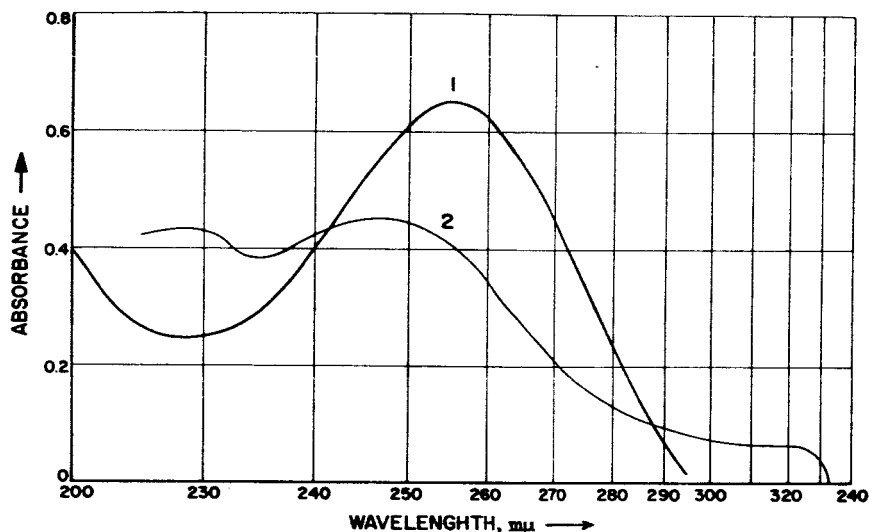


Fig. 9. Absorption spectrum of polyethylene oxide initiated with sodium-biphenyl (1) and of biphenyl (2) in DME.

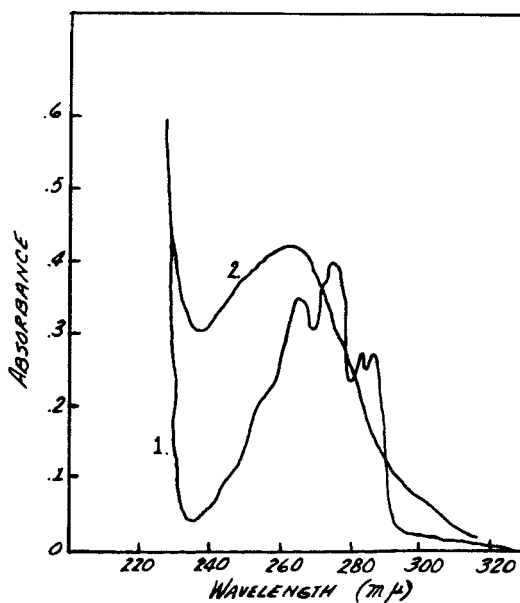


Fig. 10. Absorption spectrum of polyethylene oxide initiated by sodium-naphthalene (2) and of naphthalene (1) in DME.

the monomeric biphenyl cesium complex (1 g.) was used to initiate the polymerization of ethylene oxide (8 g.) with cesium as the alkali metal gegenion. The reaction proceeded exothermally at 0°C. and was practically completed within minutes. The polymerization rate was considerably decreased when sodium was used instead of cesium, in which case several days at 100°C. were required for complete reaction. The polyoxyethylene initiated with cesium biphenyl was obtained in practically 100% yield in the form of a white amorphous powder after precipitation from acetone with *n*-hexane. This purification method removes any free biphenyl. In Figure 9 the ultraviolet spectrum of the polymer (curve 2) confirms the hypothesis of bond formation. The appearance of an absorption band at 225–231 m μ must be due to the structural changes of the biphenyl molecule (curve 1) caused by the formation of a chemical bond between the carbon of a benzene ring and a carbon of the ethylene oxide molecule. Polyoxyethylene does not absorb in this region.

Similarly, when naphthalene alkali metal complexes were used to polymerize ethylene oxide the ultraviolet spectra of the polymer showed structural changes in the naphthalene molecule (Fig. 10).

3. Solubility and Extraction of Homopolymer

The solubility of PVB-PEO or PVN-PEO graft or block polymers varied according to composition. Grafts containing 20–80% of PEO were soluble in benzene, chloroform, tetrahydrofuran, and dimethoxyethane.

TABLE IV
Solubility of Grafts in Water

	Before extraction wt.-%	After water extraction, insoluble phase, wt.-%	wt.-% of insoluble phase	Wt.-% of extract	\bar{M}_w
PEO	75	60	53	47	
PVB	25	40			69,000
PEO	50	32	70	30	
PVB	50	68			69,000
PEO	80	67	60	40	
PVB	20	33			450,000
PEO	77	52	48	52	
PVB	23	48			60,000
PEO	77	67	69	31	
PVN	23	33			950,000

Grafts containing 10% or less of PVB were soluble in a 50:50 mixture of methanol and water. All grafts could be dissolved in a mixture of 20% methanol and 80% benzene (by volume).

The PEO homopolymer was separated from grafts containing at least 20% PVB or PVN by means of water extraction. In Table IV are shown

the weights and compositions of the insoluble phase (graft) and soluble phase (mainly PEO) after water extraction. The amount of aromatic polymer in the water extract was of the order of 1%. The molecular weight of the PEO side chains calculated on the basis of alkali metal concentration was found to be of the order of 10,000.

4. Mechanical Properties

The modulus temperature curves for pure PEO (curve 1) as well as for pure PVN (curve 2) and PVB (curve 3) are shown in Figure 11.

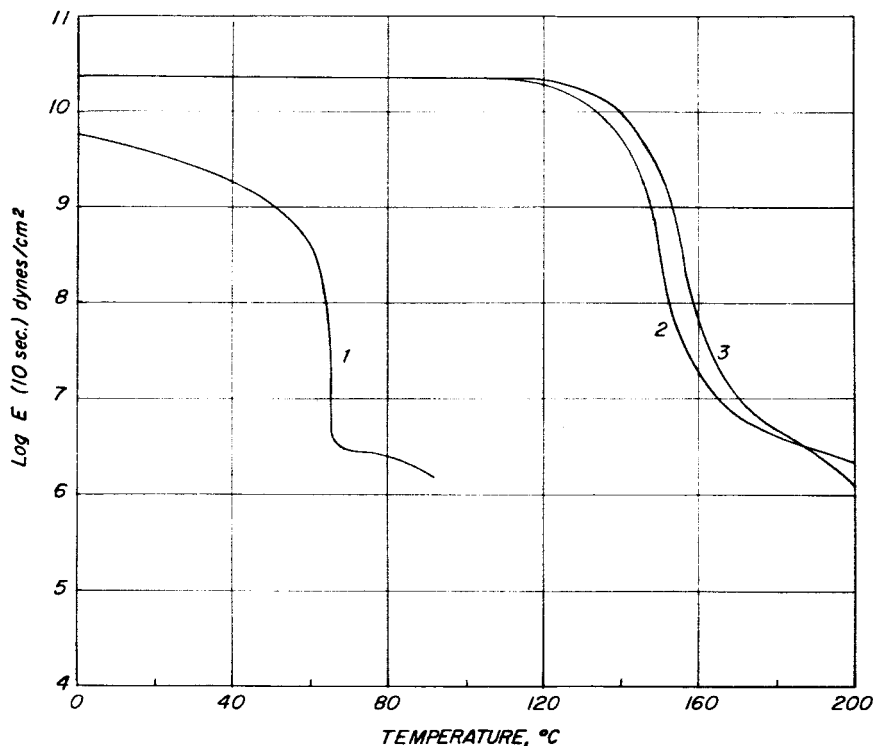


Fig. 11. Torsional modulus versus temperature for homopolymers of: (1) PEO ($\bar{M}_w = 200,000$); (2) PVN ($\bar{M}_w \sim 950,000$); (3) PVB ($\bar{M}_w = 450,000$).

The curves for PVB-PEO grafts are recorded in Figure 12, along with that for a block copolymer of the type PEO-PVB-PEO (curve 4). The weight-average molecular weight of PEO in the specimens represented by curves 2, 3, 4, and 5 was found to be of the order of 60,000–100,000. The unusual mechanical behavior of PVN-PEO grafts and blends is depicted in Figure 13. The changes in the PVN-PEO graft on heating are reflected in the modulus-temperature curve shown in Figure 14 (curve 2).

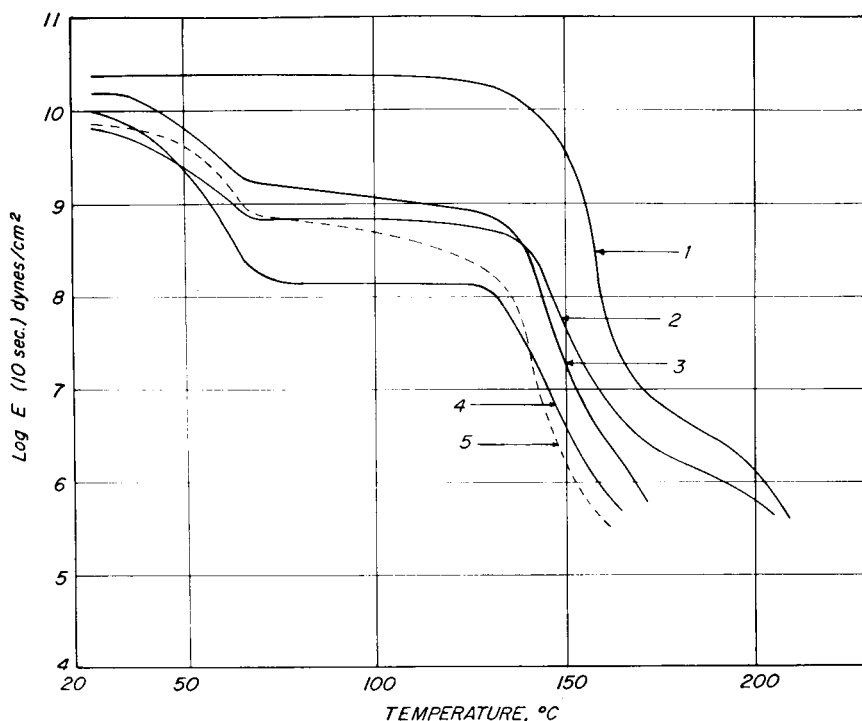
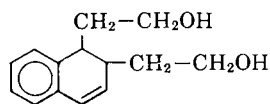


Fig. 12. Torsional modulus versus temperature for: (1) Pure PVB ($\bar{M}_w = 450,000$); (2) PVB-PEO graft (PVB 33%, PEO 67%, \bar{M}_w of PVB = 450,000); (3) PVB-PEO graft (PVB 80%, PEO 20%, \bar{M}_w of PVB = 69,000); (4) PVB-PEO block copolymer (PVB 50%, PEO 50%, M_w of PVB 60,000); (5) blend (PVB 50%, PEO 50%, \bar{M}_w of PVB 68,000).

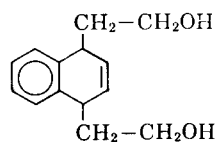
IV. INTERPRETATION OF RESULTS

1. Bond Formation

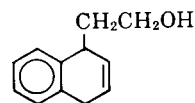
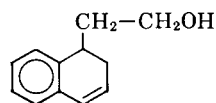
The spectroscopic results (Figs. 8–10) offer strong evidence for bond formation between ethylene oxide and biphenyl or naphthalene moieties. The isolation of pairs of isomers (I), (II), and (III) as a result of the reaction of sodium naphthalene with stoichiometric amounts of ethylene oxide completes this evidence.⁸



(I)



(II)



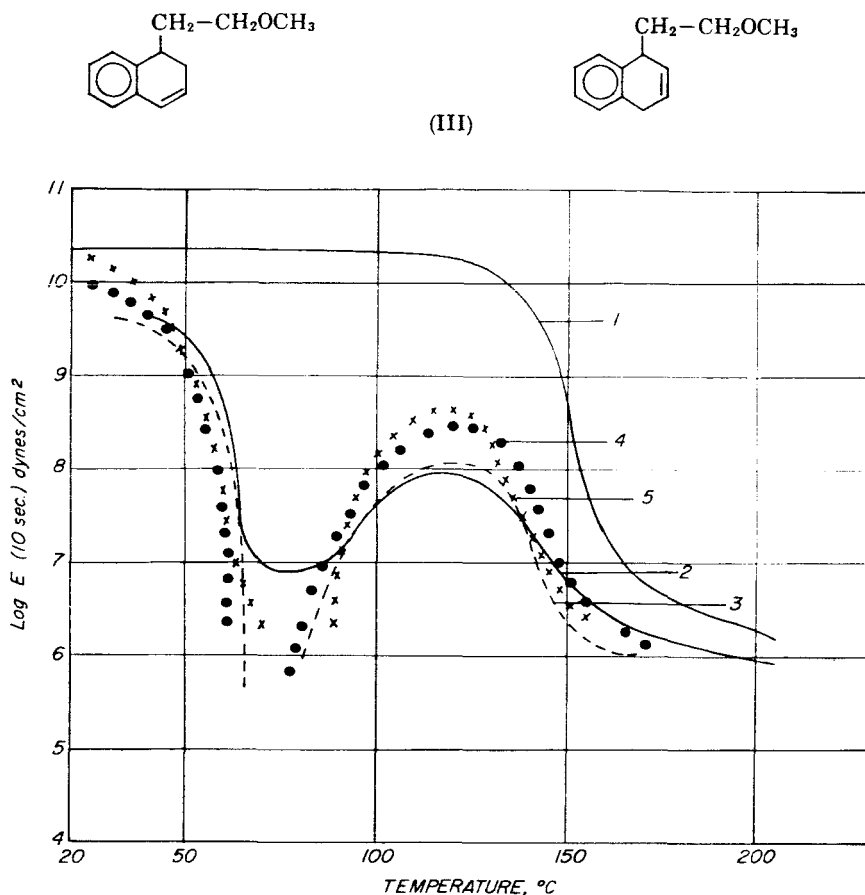


Fig. 13. Torsional modulus versus temperature for: (1) pure PVN; (2) PVN-PEO graft (PVN 25%, PEO 75%, \bar{M}_w of PVN $\approx 950,000$); (3) PVN-PEO blend (PVN 25%, PEO 75%, \bar{M}_w of PVN $\approx 950,000$); (4) PVN-PEO blend (PVN 40%, PEO 60%, \bar{M}_w of PVN $\approx 400,000$); (5) PVN-PEO blend (PVN 50%, PEO 50%, \bar{M}_w of PVN $\approx 400,000$).

The problem of bond location in a substituted biphenyl or naphthalene molecule remains to be elucidated. The experimental evidence is limited to the reaction of carbon dioxide with 2-methylnaphthalene. It was shown that 2-methylnaphthalene-Na complex reacts with CO_2 to yield 2-methyl-1,4-dihydronaphthalene-1,4-dicarboxylic acid,⁹ i.e., bond formation takes place in the substituted ring. The reaction with ethylene oxide is expected to proceed in a similar way. It is likely that both CO_2 and ethylene oxide behave as electrophilic reactants in the transition state. The point of attack would therefore depend on the π -electron densities of a substituted biphenyl or naphthalene. The π -electron densities of 1- and 2-methyl naphthalene as well as 4-methylbiphenyl radical anions were calculated by using the HMO approximation and taking into account the

inductive effect of the methyl group.¹⁰ The results of these calculations are shown in Figure 15.

The highest electron densities are likely to constitute the position of bond formation. The experimental evidence obtained so far is in agreement with these results.⁹ Assuming that the aliphatic chain in a PVB or PVN polymer exercises a similar inductive effect to a methyl group, it is possible to predict the position of bond formation with either CO₂ or ethylene oxide

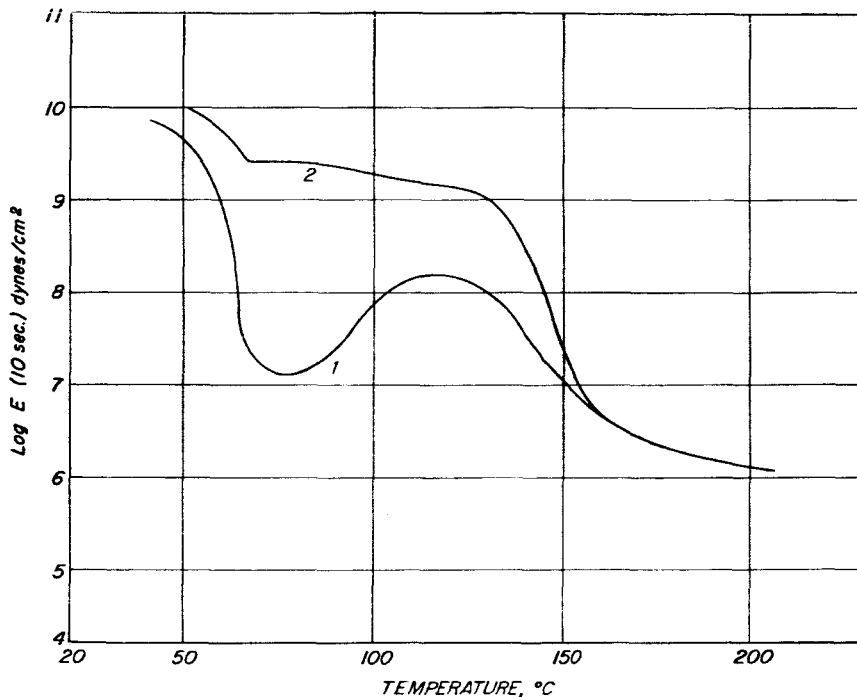
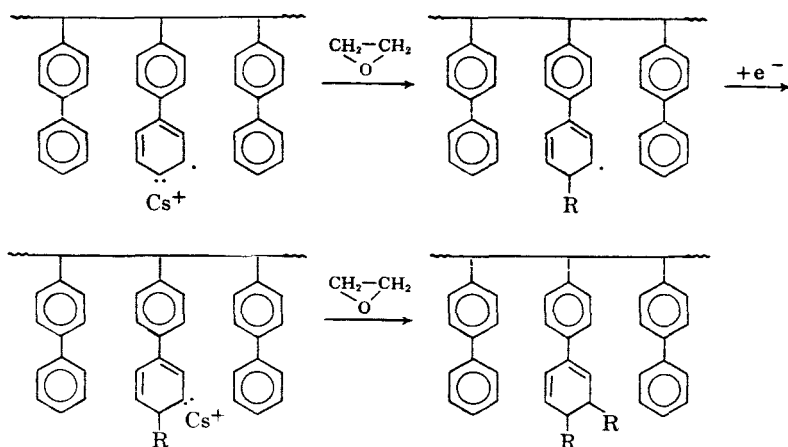


Fig. 14. Torsional modulus versus temperature for PVN-PEO graft (PVN 25%, PEO 75% M_w of PVN $\approx 950,000$): (1) before heating; (2) after heating.

in the cases where direct experimental evidence does not exist. We therefore assume that bond formation in PVB-PEO graft occurs predominantly at the 4' position of the substituted biphenyl for which the HMO calculations indicate the highest π -electron density. Similarly, addition of ethylene oxide to PVN is expected to take place at position 1 and to 1-methylnaphthalene at position 5, i.e., in the unsubstituted ring.

2. Mechanisms

The mechanism postulated by Paul, Lipkin, and Weissman¹¹ for the carbonation of the naphthalene radical anion also applies to the formation of PVB or PVN-PEO graft polymers and may be represented by the following sequence of reactions:



where R is $(\text{CH}_2-\text{CH}_2\text{O})_n \text{Cs}$.

The success of graft formation depends on the stability of polyradicalanions. The latter undergo indubitably a chain scission reaction (Table I), which leads to the formation of anions (Fig. 4). The electron spin resonance study (Figs. 5-7) substantiates the postulate of a loss of free radicals with time. In view of the above results the bond breaking mechanism is probably caused by electron migration from the aromatic rings to the α

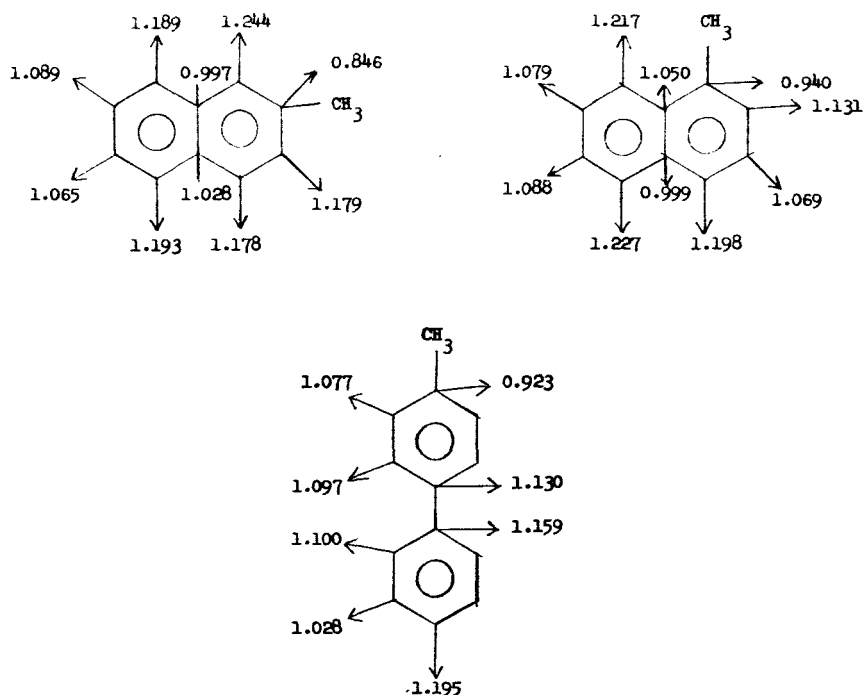
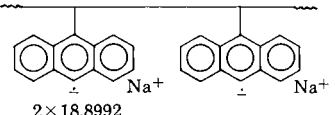
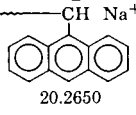
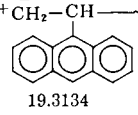
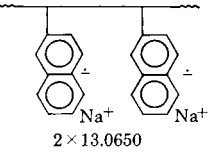
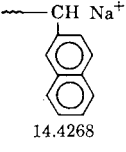
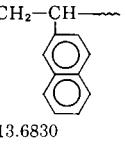
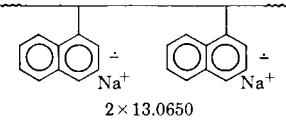
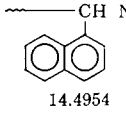
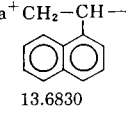
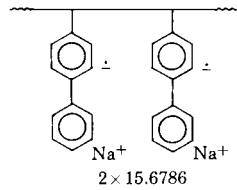
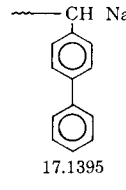
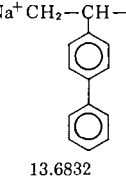
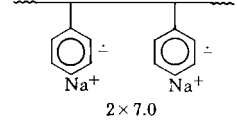
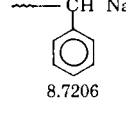
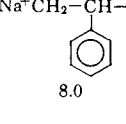
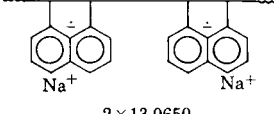
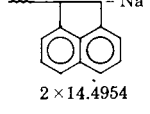
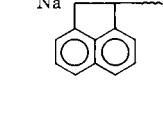


Fig. 15. π -Electron densities of methyl-substituted naphthalenes and biphenyl.

carbon atom of the aliphatic chain.¹ Additional support to the postulated electron migration mechanism is provided by considering resonance energies of the various species. The resonance energies of some radical anions and the corresponding anions, shown in Table V, were calculated by the Huckel molecular orbital approximation. The difference in energies is an indication of the relative stability of the various species.

If we assume that resonance stabilization is the main factor in the formation of anions from polyradicalanions, then Table V implies that the tend-

TABLE V
 π -Resonance Energy Gain after Bond Scission

Polyradicalanion	Anions	Energy gain β
 2×18.8992	 $\text{Na}^+ \text{CH}_2\text{---CH}$  20.2650 19.3134	1.7800
 2×13.0650	 $\text{Na}^+ \text{CH}_2\text{---CH}$  14.4268 13.6830	1.9798
 2×13.0650	 $\text{Na}^+ \text{CH}_2\text{---CH}$  14.4954 13.6830	2.0484
 2×15.6786	 $\text{Na}^+ \text{CH}_2\text{---CH}$  17.1395 13.6832	2.1655
 2×7.0	 $\text{Na}^+ \text{CH}_2\text{---CH}$  8.7206 8.0	2.7206
 2×13.0650	 $\text{Na}^+ \text{CH}_2\text{---CH}$  2×14.4954 2.8608	2.8608

ency of anion formation should increase from poly-9-vinylanthracene which would be expected to be the most stable, to polyacenaphthylene likely to be the least stable. This is in agreement with the experimental results obtained so far. Thus polyacenaphthylene undergoes chain scission instantaneously while PVB and PVN undergo degradation at a measurable rate even at a temperature of 75°C. (Figs. 2 and 3).

It is possible therefore to stabilize the PVB and PVN polyradicalanions at lower temperatures and form grafts with monomers, provided bond formation and not electron transfer is occurring.

3. Solubility and Formation of Homopolymer

Although quantitative polymerization yields could be obtained from all experiments, large amounts of PEO homopolymer were isolated by water extraction in all cases (Table IV). The main reason for homopolymer formation is the presence of impurities capable of reacting with metallic cesium to form initiators for the polymerization of ethylene oxide. A yield of 10% of PEO was obtained by first reacting purified THF with a metallic cesium mirror and then carrying out the subsequent steps as for the preparation of grafts, but in absence of the aromatic polymer.

4. Mechanical Properties

The modulus-temperature curves for the PEO, PVB, and PVN homopolymers are shown in Figure 11. As PEO is heated, at first the modulus decreases gradually in a way characteristic of slow melting in crystalline polymers, until about 65°C. a sharp melting point is reached. The length of the plateau which extends beyond the melting temperature depends on the molecular weight of the polymer. Both PVB and PVN exhibit a constant glassy modulus for low temperatures, and then go through the transition region rather rapidly, as expected for amorphous polymers. It is to be noted that PVB, although having lower molecular weight (450,000 vs. 1,000,000), exhibits a slightly higher T_g than PVN (ca. 154 vs. 148°C.).

The curve for PVB (curve 1) is reproduced in Figure 12 along with those for two PVB-PEO grafts (curves 2 and 3), a block (curve 4), and a blend (curve 5). The two-component systems exhibit two transitions, one corresponding to the melting of PEO (ca 65°C.) and the other to the glass transition of PVB (130–150°C.). This behavior is similar to that of polystyrene-butadiene blends,¹² but in the presence of appreciable amounts of low molecular weight PEO, only the first transition is observed. The modulus in the intermediate zone 65–130°C., is proportional to the PVB content and is at a level characteristic of leathery behavior. For high molecular weight PVB (curve 2) a plateau is exhibited, whereas for low molecular weights the modulus gradually decreases (curve 3). This is not surprising, since PVB is now imbedded in liquid PEO and its mobility should depend primarily on the extent of entanglement with its own species. The latter in turn depends on the molecular weight of PVB. The extension of the PVB chain at both ends in the block polymer sufficiently in-

creased entanglement for the system to exhibit a plateau, although the molecular weight of the PVB portion is only about 60,000. Differences between blends and grafts are not apparent. Qualitative observations, however, indicate that the modulus in the leathery zone relaxes at a faster rate for blends than for grafts. More quantitative observations of time-temperature-dependent behavior are planned in order to assess these differences.

For the PVN-PEO systems (Fig. 13) the modulus-temperature curves exhibited a very unusual behavior. A "well" was observed in the intermediate zone, instead of a plateau. Past the minimum of the well the modulus rises until a maximum is reached at about 120°C., and then decreases as the specimen goes through the transition of PVN. This behavior is exhibited by both blends and grafts, although the well is shallower for the latter. Also, in order to follow the equilibrium curve the temperature had to be changed more gradually for grafts than for blends. Again this strongly suggests markedly greater mobility of chain motions in blends than in grafts.

Although the exact reason for the well behavior is not known, certain experimental observations may be used to offer a plausible explanation. At room temperature the specimen is opaque. As the PEO melts (>65°C.) the specimen becomes transparent, but on further temperature increase (about 80°C.) becomes opaque again. This indicates that at first PVN dissolves in PEO, but as the temperature increases it starts to precipitate out, thus raising the modulus by acting as a filler. Once a specimen had been exposed to a temperature of 120°C. the well behavior is lost, and a behavior similar to that of the PVB systems is exhibited, as illustrated in Figure 14, where the modulus curve of a preheated specimen is shown together with the original curve.

The test specimens are molded at temperatures (100–110°C.) below T_g of PVN, and since the molding powder was obtained by precipitation at room temperature with a nonsolvent from a relatively dilute solution, it follows that the PVN chains are "frozen" in a compact configuration characteristic of the conditions under which they were precipitated. Visual observations indicate that PVN chains in this configuration exhibit maximum solubility in melted PEO at about 65°C. Once the temperature of about 120°C. is exceeded, PVN can uncoil and entangle with the surrounding chains from both PEO and other PVN segments. The exact temperature range depends on both composition and molecular weight. These considerations are consistent with the observed dependence of crystallinity on thermal history. When molded specimens were examined with polarized light, crystalline PEO spherulites could be seen before but not after heating above 120°C.

The factors needed for the well behavior to be exhibited must be quite critical and appear to be related to the thermodynamics of the two-component system. The phenomenon almost certainly depends on the phase relations between PEO and the aromatic system. Although we still lack

data on this point, it is significant that dimethoxyethane, an ether structurally similar to PEO, is a markedly better solvent for PVB than for PVN, and this is consistent with the fact that none of the PVB systems exhibited the unusual "well" phenomenon.

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Synopsis

The aromatic moieties of vinyl polymers such as poly-4-vinylbiphenyl and poly-2-vinylnaphthalene react in solution with alkali metals to form colored charge-transfer complexes. These polymers, referred to as polyradicalanions, initiate the polymerization of ethylene oxide by bond formation, thus leading to the formation of graft polymers. The polyradicalanions, however, may degrade at ambient temperature into polymeric anions. Therefore, to prepare graft polymers one has to select suitable polymer systems as well as reaction conditions which minimize the degradation process. Graft and block copolymers having poly-4-vinylbiphenyl or poly-2-vinylnaphthalene backbones and polyethylene oxide branches were prepared, and the properties of these compared to those of homopolymers and blends. The preparations were characterized by their solubility behavior as well as by chemical and spectral analyses. The mechanical properties were investigated by means of torsional modulus vs. temperature measurements. The reaction mechanisms and relative stabilities of the various species are discussed in terms of molecular orbital calculations. For the poly-2-vinylnaphthalene grafts and blends the modulus exhibited a minimum at about 65°C. A tentative explanation is offered for this phenomenon.

Résumé

Les parties aromatiques des polymères vinyliques tels que le poly-4-vinyl-biphényle et le poly-2-vinylnaphtalène réagissent en solution avec des métaux alcalins pour former des complexes colorés à transfert de charge. Ces polymères, appelés anions polyradicalaires, initient la polymérisation de l'oxyde d'éthylène par formation de liens, conduisant ainsi à la formation de polymères greffés. Les anions polyradicalaires cependant, peuvent se dégrader à température ambiante en anions polymériques. Dès lors, pour préparer des copolymères greffés, il faut choisir des systèmes polymériques adaptés ainsi que des conditions de réaction qui minimisent le processus de dégradation. On a préparé des copolymères greffés et séquencés ayant comme chaîne principale le poly-4-vinylbiphényle ou le poly-2-vinylnaphtalène et comme greffons de l'oxyde de polyéthylène et leurs propriétés sont comparées à celles des homopolymères et des mélanges.

Les produits préparés ont été caractérisés par leur solubilité ainsi que par analyse chimique et spectrale. Les propriétés mécaniques ont été étudiées au moyen de mesures du module de torsion en fonction de la température. Les mécanismes des réactions et les stabilités relatives des différentes espèces sont discutés en termes de calculs d'orbitales moléculaires. Pour les poly-2-vinylnaphtalènes greffés et en mélange, le module présente un minimum aux environs de 65°C. On essaie de donner une explication à ce phénomène.

Zusammenfassung

Die aromatischen Gruppen von Vinylpolymeren, wie Poly-4-vinylbiphenyl und Poly-2-vinylnaphthalin, reagieren in Lösung mit Alkalimetallen unter Bildung gefärbter "charge-transfer"-Komplexe. Diese, als Polyradikalanionen bezeichnete Polymeren starten die Polymerisation von Äthylenoxyd, indem sie eine Bindung zu diesem ausbilden und so zu Pfropfpolymeren führen. Die Polyradikalanionen können aber bei Raumtemperatur zu polymeren Anionen abgebaut werden. Um daher Pfropfpolymeren darzustellen, muss man sowohl geeignete Polymersysteme wie auch Reaktionsbedingungen mit geringst möglichem Abbau auswählen. Pfropfund Blockcopolymeren mit einer Poly-4-vinylbiphenyl- oder Poly-2-vinylnaphthalin-Hauptkette und Polyäthylenoxyd-Seitenketten wurden dargestellt und ihre Eigenschaften mit denen von Homopolymeren und deren Mischungen verglichen. Die Präparate wurden durch ihr Löslichkeitsverhalten, wie auch durch chemische Analyse und Spektralanalyse charakterisiert. Die mechanischen Eigenschaften wurden anhand von Messungen des Torsionsmoduls in Abhängigkeit von der Temperatur untersucht. Der Reaktionsmechanismus und die relative Stabilität der verschiedenen Stoffe werden auf Grundlage von Molekülorbitalberechnungen diskutiert. Bei Poly-2-vinylnaphthalin-Aufpfropfungen und Mischungen zeigte der Modul ein Minimum bei etwa 65°C. Eine vorläufige Erklärung dieser Erscheinung wird gegeben.

Discussion

N. A. Plate (*Université de Moscow, Moscow, U.R.S.S.*): (1) Can you say anything about the kinetics of graft polymerization of your systems compared with the kinetics of polymerization catalyzed by sodium-naphthalene complexes? (2) What is the microtacticity of your polymers and did you work with polymers of different microstructure?

A. Rembaum: We have observed that when using sodium as the counter-ion the propagation step is very slow even at 100°C. By the use of a well defined cesium concentration, the graft polymerization is practically over within thirty minutes at 0°C., we did not study the detailed reaction kinetics.

M. Gole (*Institut National des Sciences Appliquées, Lyon, France*): Nous avons travaillé en collaboration avec Corbière et Rempp dans le même domaine depuis trois ans et les résultats que nous avons obtenus sont très semblables à ceux de Rembaum. Je voudrais seulement poser quelques questions pratiques: (1) Quels sont les taux de sodation obtenus? (2) La dégradation est fonction de la température, est-elle aussi fonction du taux de métallation?

A. Rembaum: The extent of electron transfer from the alkali metal to the aromatic polymer depends on the reaction time and also on the molecular weight and polymer concentration. We found it difficult to form polyradicalanions in concentrated and viscous solutions. Using longer reaction times and more dilute solutions, a high alkali concentration may be achieved. Our polymer contained between 3 to about 30 mole-% of alkali metal.

Teh Fu Yen (*Mellon Institute, Pittsburgh, Penna.*): The positions of bond formation for the graft polymer are consistent with our observation of those of the polymers containing aromatic hydrocarbons prepared by condensation with formaldehyde. In the case of α -methyl naphthalene, the propagation is through 5,8. In the case of the β -isomer, the

propagation is through 1,5. We also observed a shift to higher wave length of the UV-visible spectra of those polymers when compared to those of the parent hydrocarbons.

A. Rembaum: It is very gratifying to hear this.

P. Rempp (*C. R. M., Strasbourg, France*): Did you carry out systematic determinations of the molecular weight of your polymeric system, as a function of their degrees of metallation?

A. Rembaum: We investigated the rate of polymer degradation by viscosimetry as a function of sodium concentration and temperature. We followed the changes of absorption intensities in the visible and the decrease of the intensity of the electron spin resonance signal with time. We have also isolated polymer samples after reaction with a known amount of sodium at different times and determined their molecular weight by light scattering or viscosity measurements.

M. Goutiere (*France*): (1) Quelle est la façon de désactiver le polyvinylnaphtalène métallé? (2) Pour notre part nous avons utilisé le méthanol et nous avons observé une légère réticulation. Dans le cas- d'un polyvinyl naphtalène de haute masse moléculaire cette réticulation s'explique par le fait que la désactivation transforme un noyau naphtyle en dehydro-naphtle, et que celui-ci est nitrable par le naphtalène sodium restant.

A. Rembaum: We used methanol or methyl iodide for the termination reaction and did not observe any crosslinking in either case. Your observation of insoluble polymer formation may be due to the high sodium concentration which could lead to dianions rather than to radical anions.